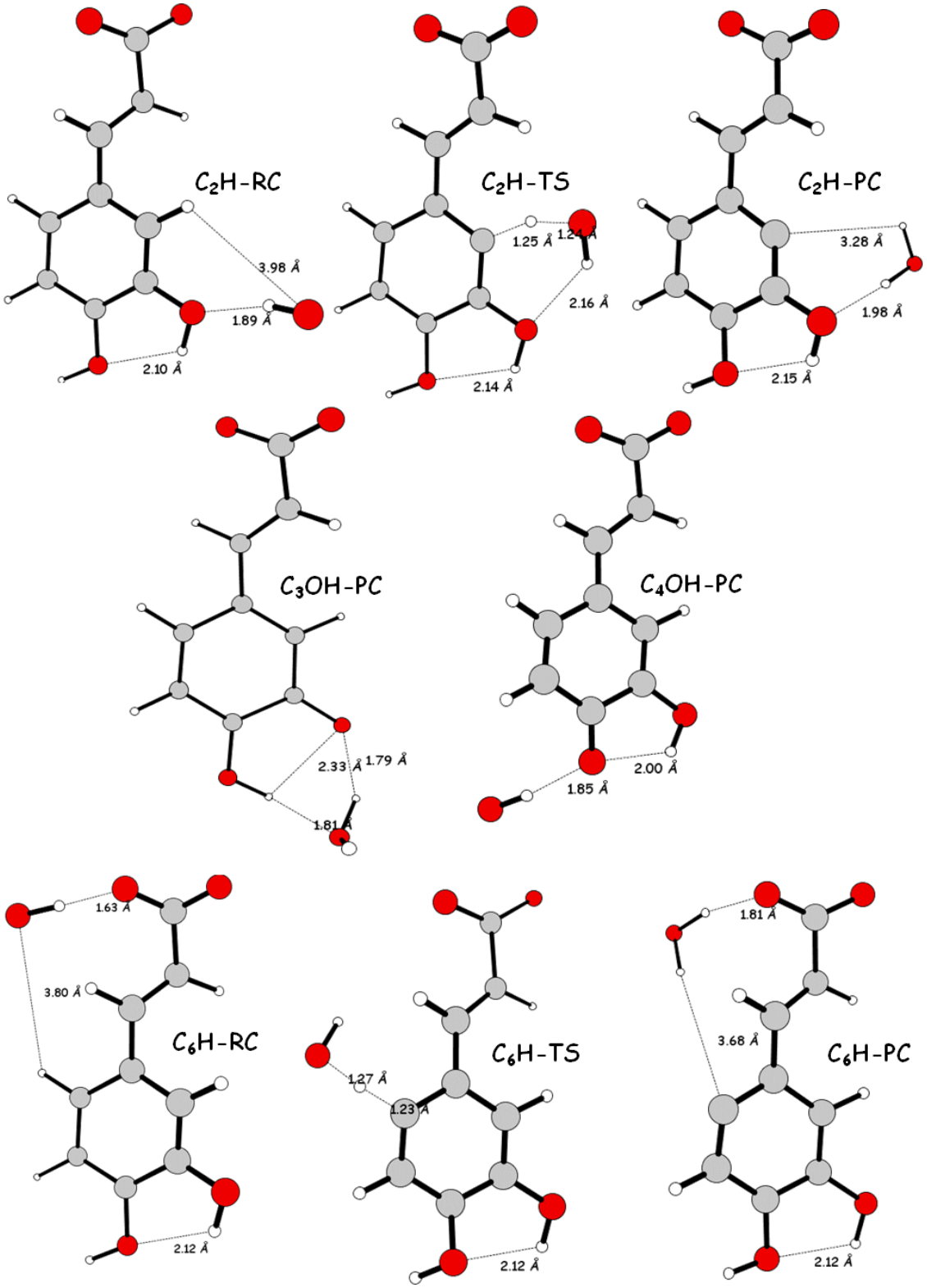
SUPPORTING INFORMATION



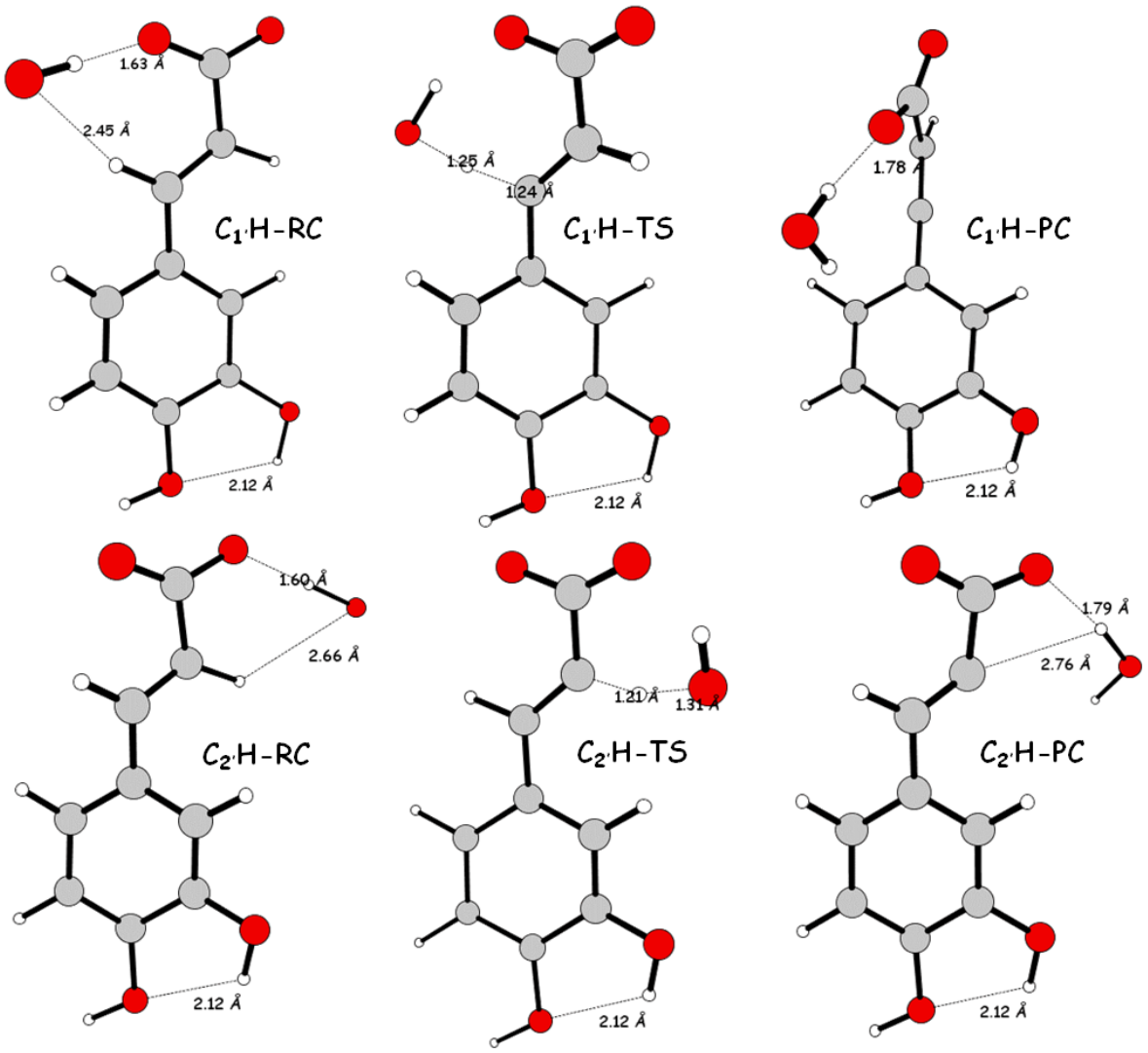
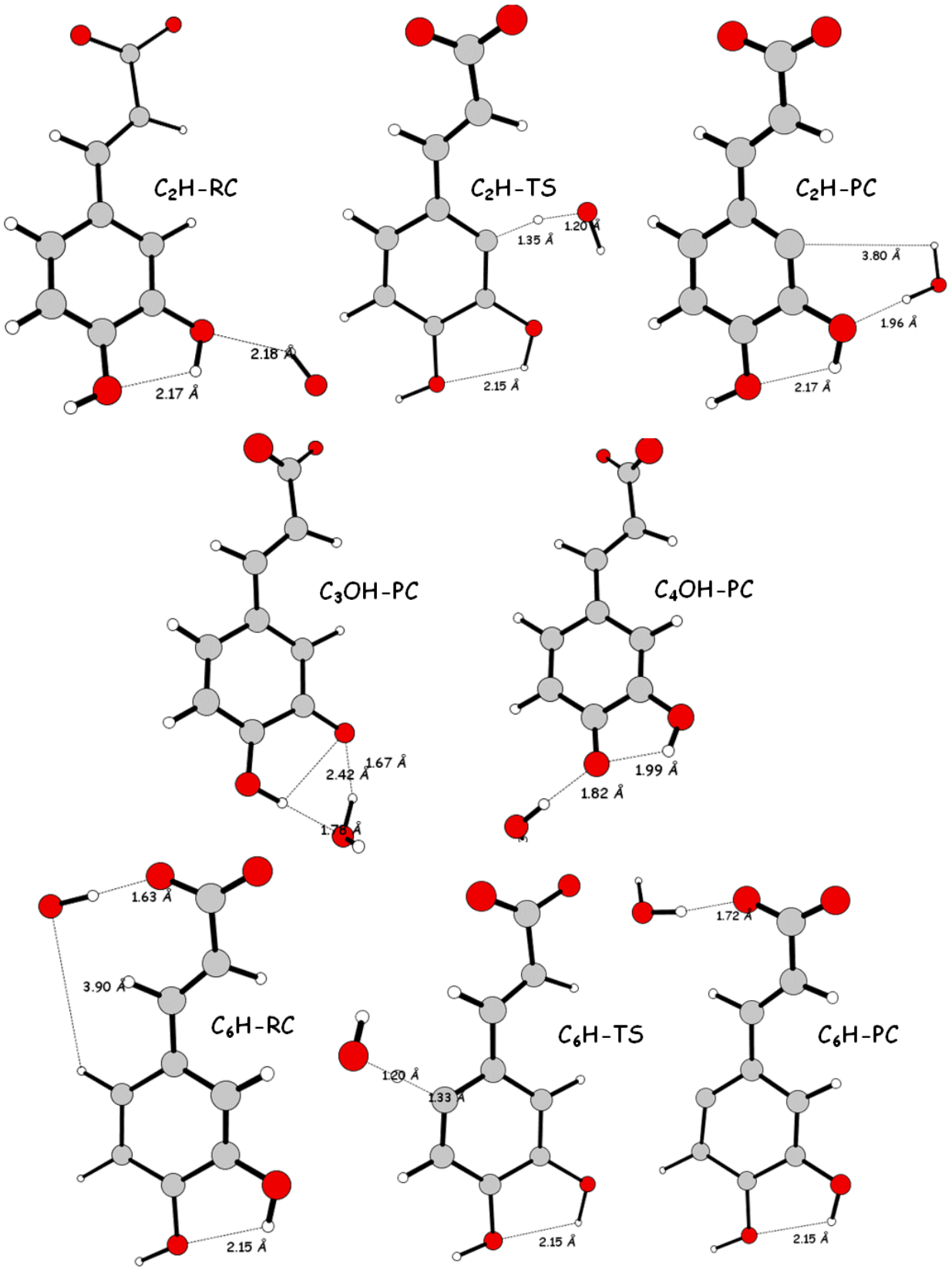


Figure S1. M05-2X optimized geometries of the stationary points encountered along the HAT mechanism for the anion of caffeic acid.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C3OH-PC
1.67 Å
2.42 Å
1.78 Å
C4OH-PC
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1.82 Å
C6H-RC
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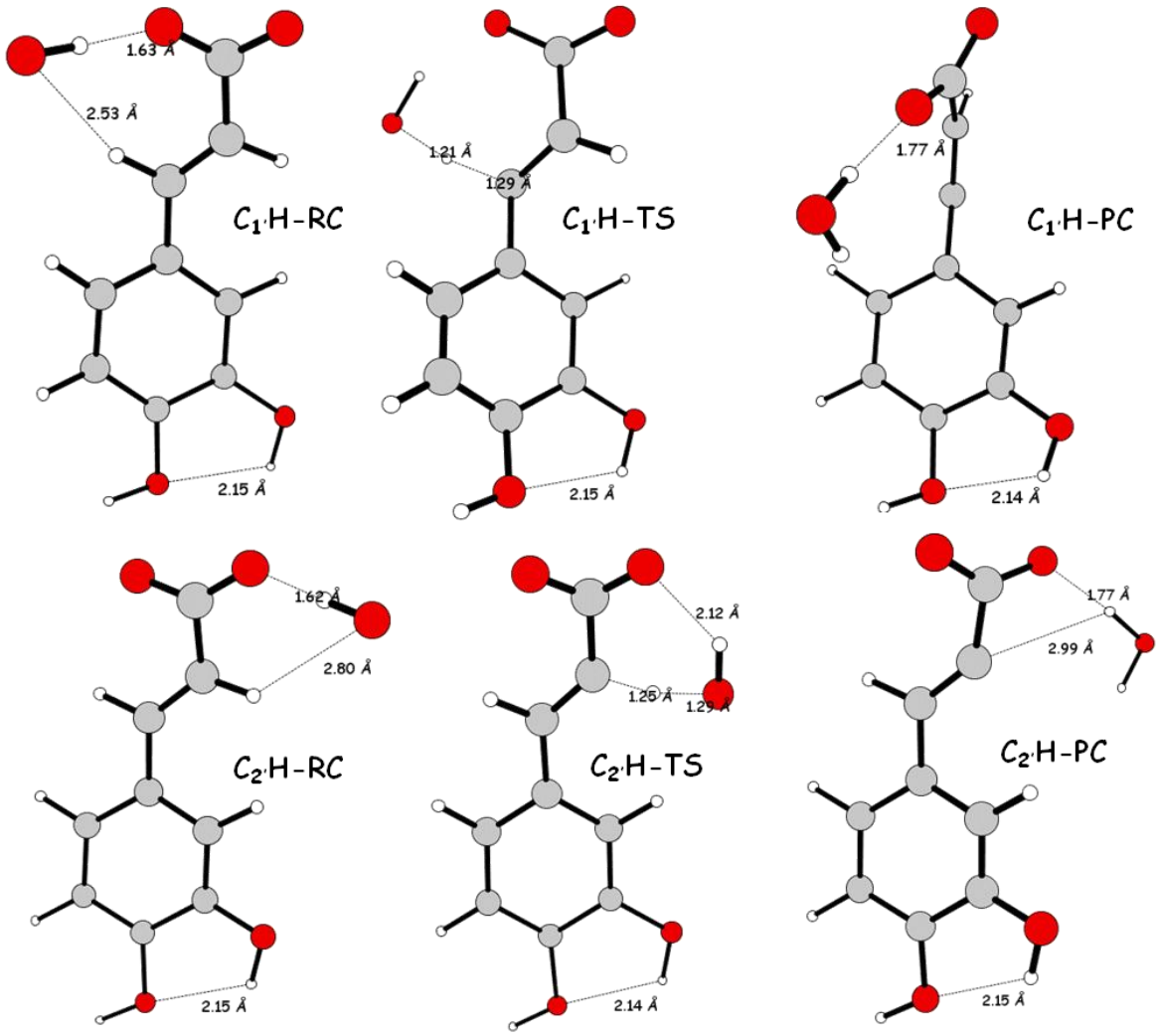
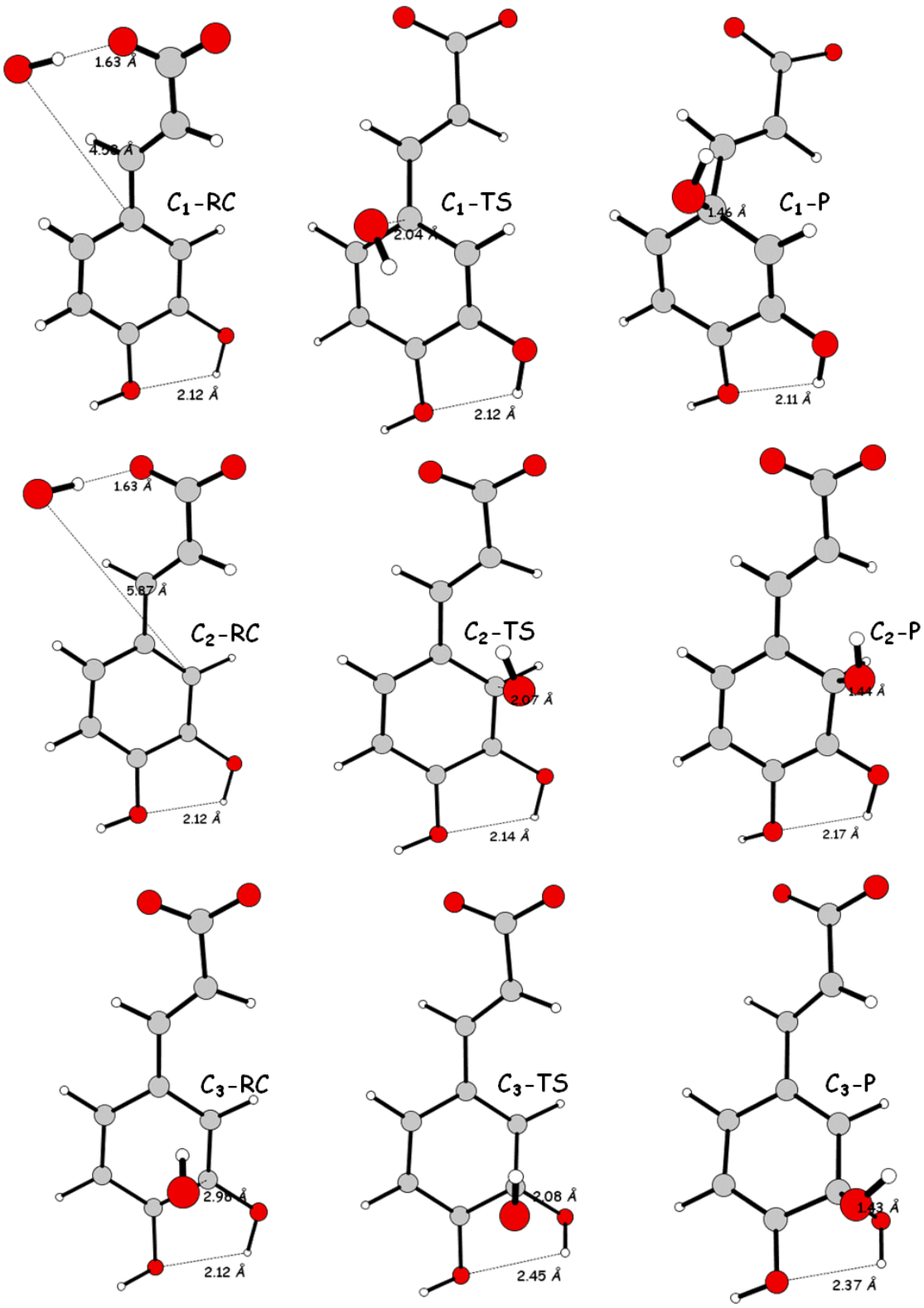


Figure S2. B3LYP optimized geometries of the stationary points encountered along the HAT mechanism for the anion of caffeic acid.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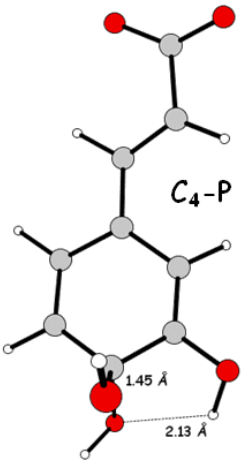
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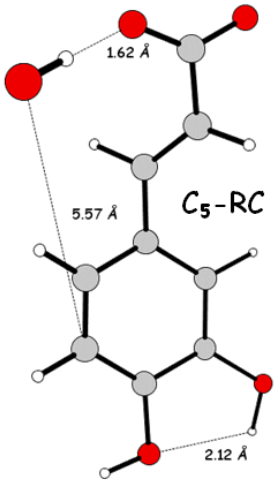
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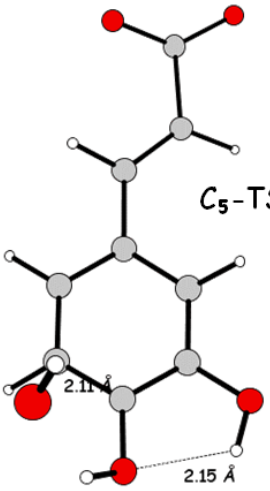
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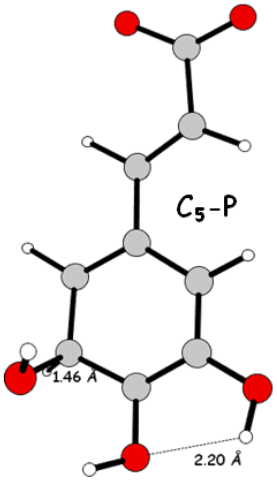
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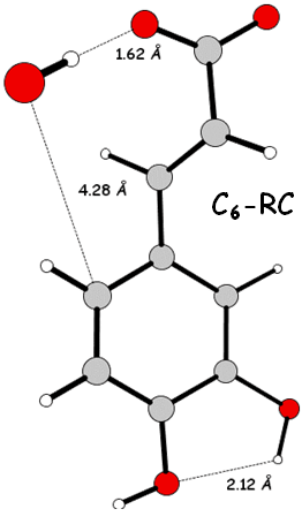
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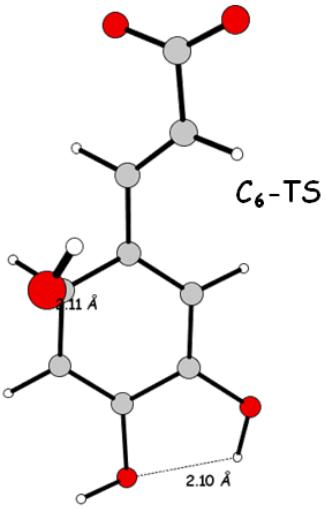
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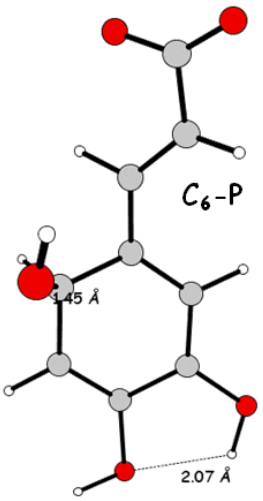
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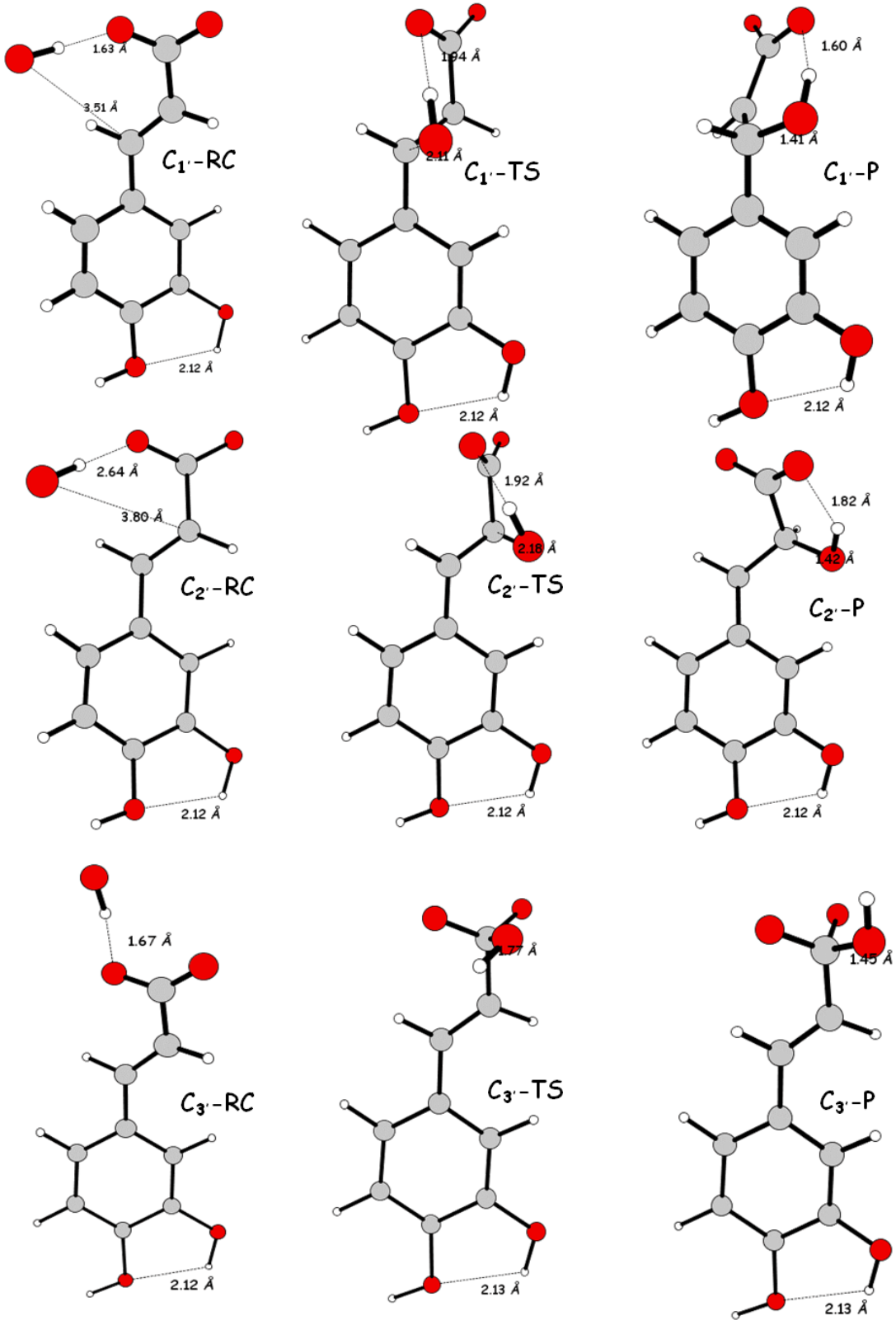
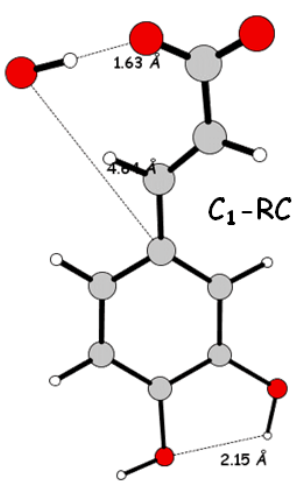


Figure S3. M05-2X optimized geometries of the stationary points encountered along the RAF mechanism for the anion of caffeic acid.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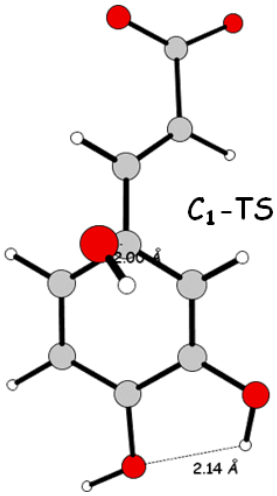
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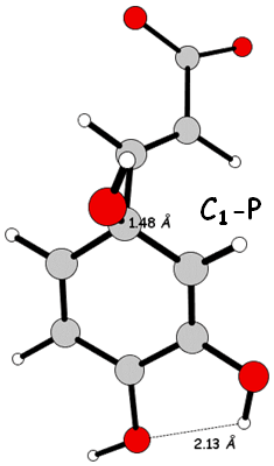
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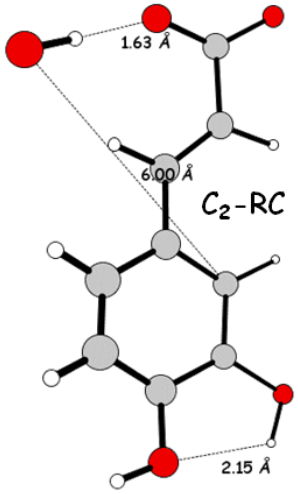
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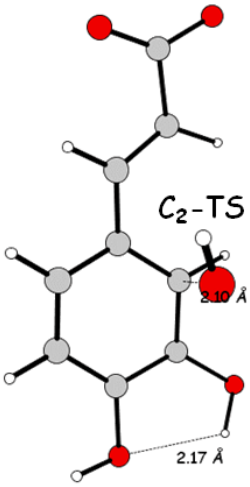
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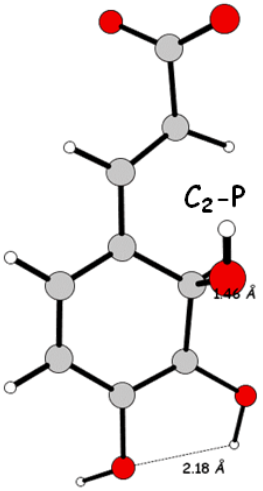
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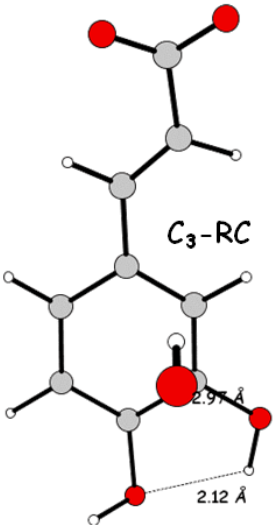
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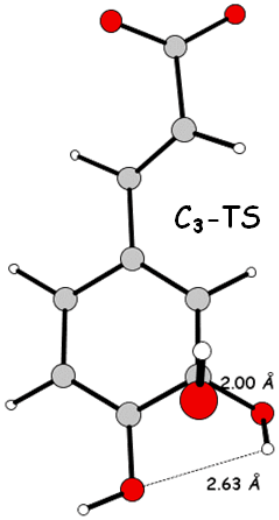
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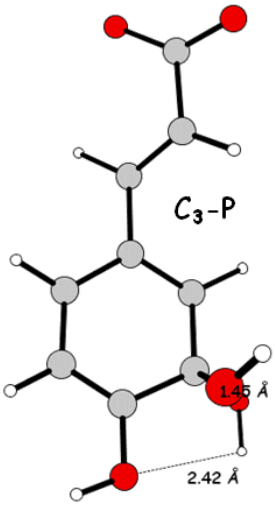
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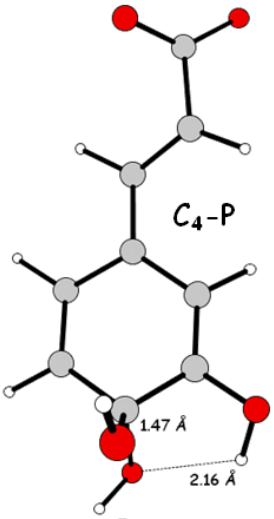
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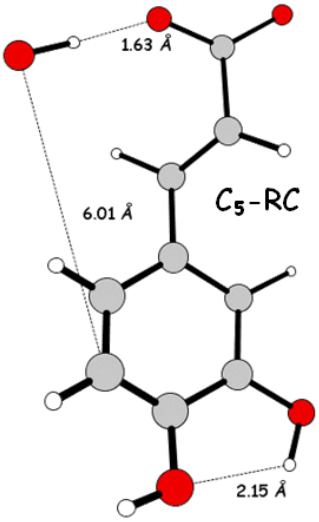
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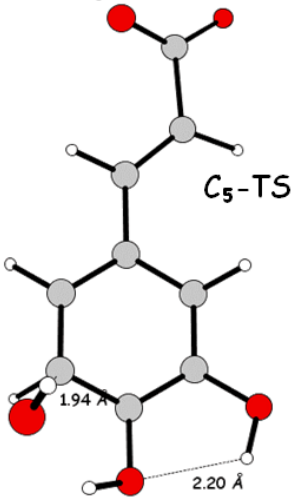
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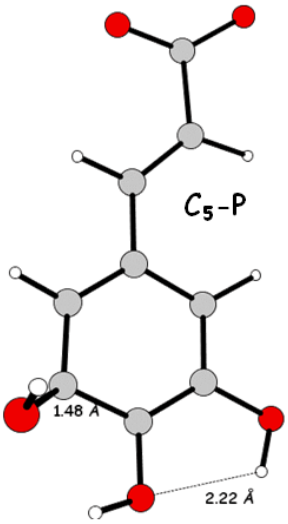
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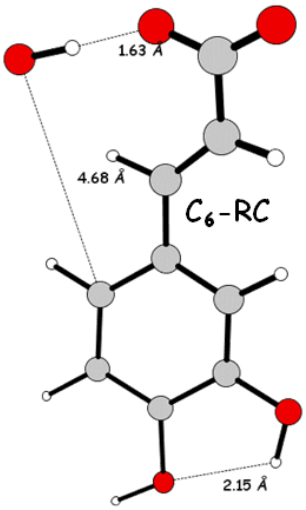
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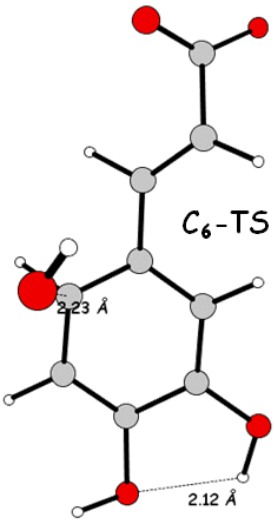
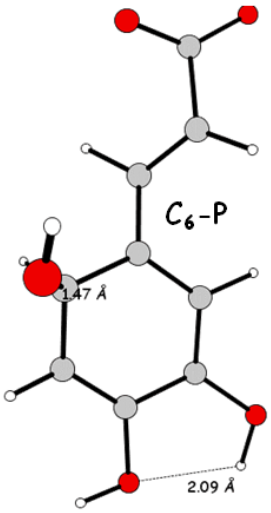

C6-TS
2.23 Å
2.12 Å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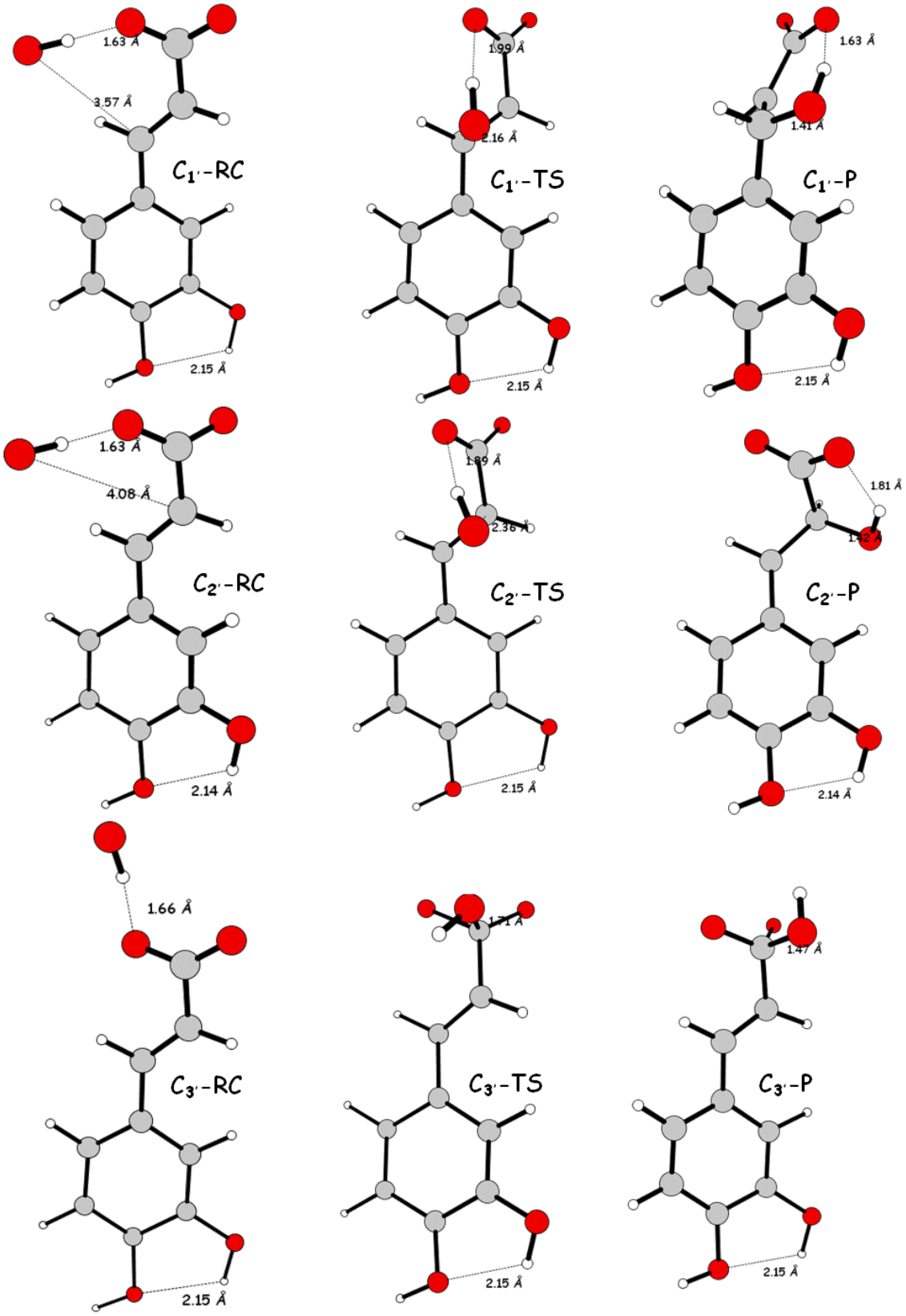

Figure S4. B3LYP optimized geometries of the stationary points encountered along the RAF mechanism for the anion of caffeic acid.

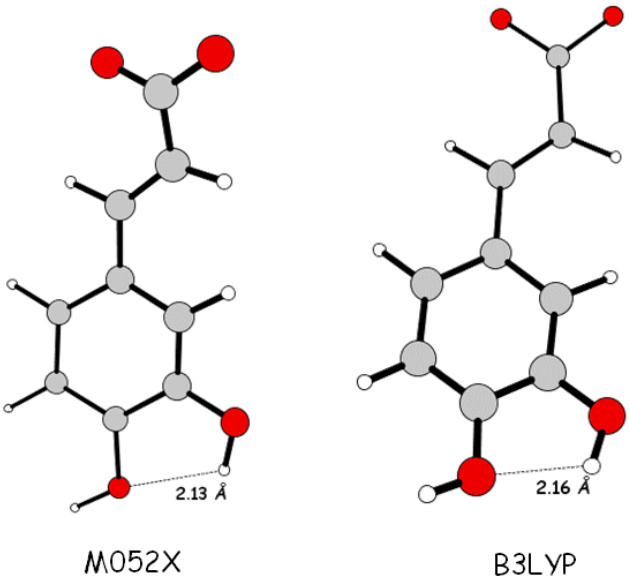

Figure S5. M05-2X and B3LYP optimized geometries of the radical cation arising from SET mechanism for the anion of caffeic acid.

Table S1. Atomic spin densities (in |e|) at the M05-2X level in the product complex for HAT mechanism

	Channel							
Atom	**C_2H**	**C_3OH**	**C_4OH**	**C_5H**	**C_6H**	**$C_1{\cdot}H$**	**$C_2{\cdot}H$**	**$C_3{\cdot}OOH$**
C_1	-0.15961	-0.09190	0.35840	0.12295	0.02198	-0.25421	0.23357	0.00930
C_2	0.91632	0.15416	-0.15883	-0.09098	0.05625	0.24099	0.01957	-0.00107
C_3	-0.00757	0.01627	0.27126	0.09421	-0.03716	-0.10662	0.02791	0.00009
C_4	0.10068	0.29801	0.02629	-0.32528	0.11061	0.23862	-0.03165	0.00814
C_5	-0.05785	-0.13916	0.20569	1.08631	-0.25895	-0.11451	0.01687	-0.00214
C_6	-0.15961	0.31274	-0.14982	0.06726	0.85749	0.23336	-0.09176	0.00422
C_1'	0.11313	0.04296	-0.16997	-0.01545	0.21647	0.84312	-0.63077	-0.02755
C_2'	-0.03347	-0.00529	0.24879	0.00773	0.00297	-0.14987	1.26529	0.06151
C_3'	0.00863	0.00427	-0.01650	0.00033	-0.00132	0.03403	0.04960	-0.17348
O_{C3}	0.00463	0.33639	0.06258	0.00834	-0.00525	-0.00813	0.00100	0.00011
O_{C4}	0.00104	0.09136	0.28550	0.00983	0.00672	0.02262	-0.00260	0.00201
O_{OH}	0.02758	0.00172	0.00115	0.00742	0.00591	0.00154	0.00640	-0.00028
O_{1COOH}	-0.00381	0.00010	0.04149	0.00172	-0.00541	-0.01500	0.06388	0.24946
O_{2COOH}	-0.00065	-0.00000	0.00488	0.00036	-0.00083	-0.00104	0.00884	0.87112

Table S2. Atomic spin densities (in |e|) at the M05-2X level in the product for RAF mechanism

	Channel								
Atom	**C_1**	**C_2**	**C_3**	**C_4**	**C_5**	**C_6**	**C_1'**	**C_2'**	**C_3'**
C_1	-0.01364	0.41867	-0.31072	0.47525	-0.19626	0.48973	-0.04614	-0.28862	0.00298
C_2	0.30484	-0.00347	0.49416	-0.14349	0.57145	-0.20631	-0.03640	0.24182	0.00890
C_3	-0.16243	0.35076	-0.02058	0.28517	-0.27000	0.40731	0.02102	-0.08489	-0.00094
C_4	0.52720	-0.17429	0.37513	-0.00834	0.49897	-0.11455	-0.00260	0.23512	0.00428
C_5	-0.22187	0.47880	-0.21592	0.32621	-0.12651	0.24159	0.02262	-0.11266	-0.00142
C_6	0.49720	-0.28102	0.57728	-0.21329	0.45214	-0.10071	0.05414	0.24345	0.00370
C_1'	-0.00514	-0.16386	0.14613	-0.20523	0.05628	-0.17663	-0.08482	0.82671	0.03446
C_2'	0.03072	0.23321	-0.08005	0.35739	-0.05139	0.30547	0.90970	-0.03636	-0.02908
C_3'	0.00014	0.00413	0.00427	-0.01153	0.00648	-0.00766	-0.03508	-0.02657	-0.02964
O_{C3}	-0.00766	0.06035	0.01700	0.04815	-0.01010	0.06335	0.00069	-0.00761	-0.00016
O_{C4}	0.05415	-0.00480	0.04250	0.01156	0.04652	-0.00369	-0.00014	0.02142	0.00051
O_{OH}	0.01820	0.02657	0.02051	0.01891	0.02054	0.02449	0.02605	0.00829	0.09230
O_{1COOH}	0.00660	0.03983	-0.01322	0.06485	-0.01051	0.05685	0.15482	0.00356	0.91096
O_{2COOH}	0.00089	0.00509	-0.00178	0.00836	-0.00160	0.00764	0.02148	-0.00204	0.00614

Table S3. Atomic spin densities (in |e|) at the M05-2X level in the product for SET mechanism

Atom	
$\mathbf{C_1}$	0.20278
$\mathbf{C_2}$	-0.11981
$\mathbf{C_3}$	0.12584
$\mathbf{C_4}$	0.30948
$\mathbf{C_5}$	-0.07497
$\mathbf{C_6}$	0.18402
$\mathbf{C_{1'}}$	-0.15091
$\mathbf{C_{2'}}$	0.36649
$\mathbf{C_{3'}}$	-0.04284
$\mathbf{O_{C3}}$	0.06259
$\mathbf{O_{C4}}$	0.09681
$\mathbf{O_{1COOH}}$	0.00230
$\mathbf{O_{2COOH}}$	-0.01466

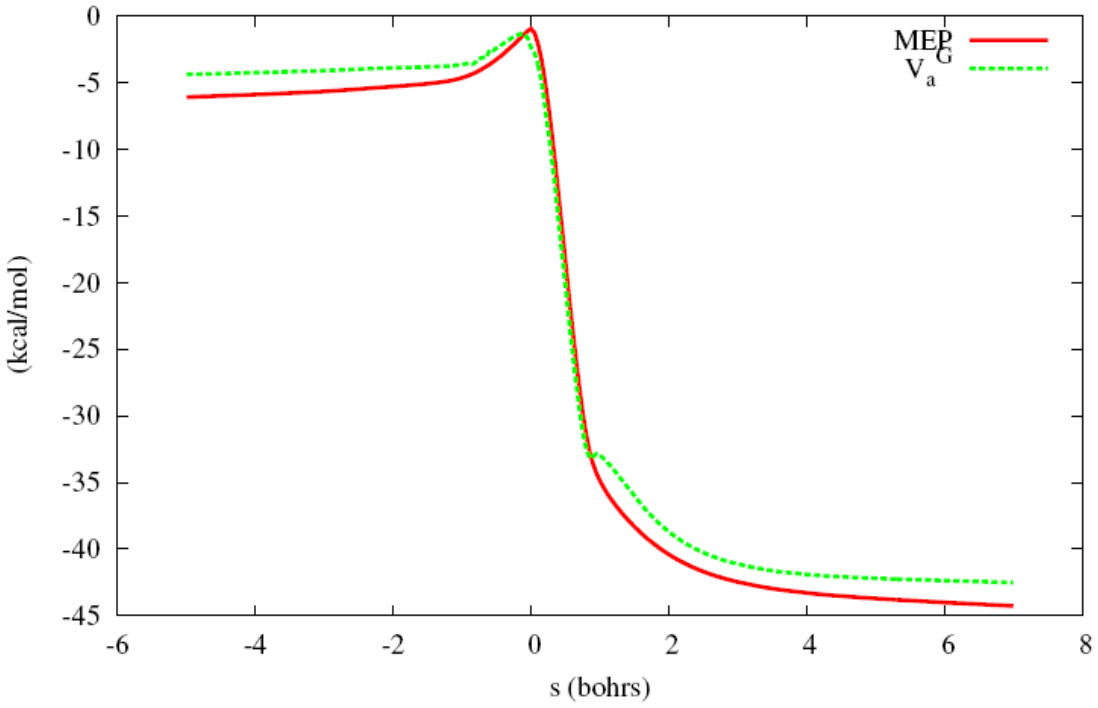

Figure S6. Minimum Energy Path (V_{MEP}) and Adiabatic (V_a^G) potential-energy profiles computed at M052X level of theory for the HAT mechanism between the 4OH site of caffeic acid and the OH radical

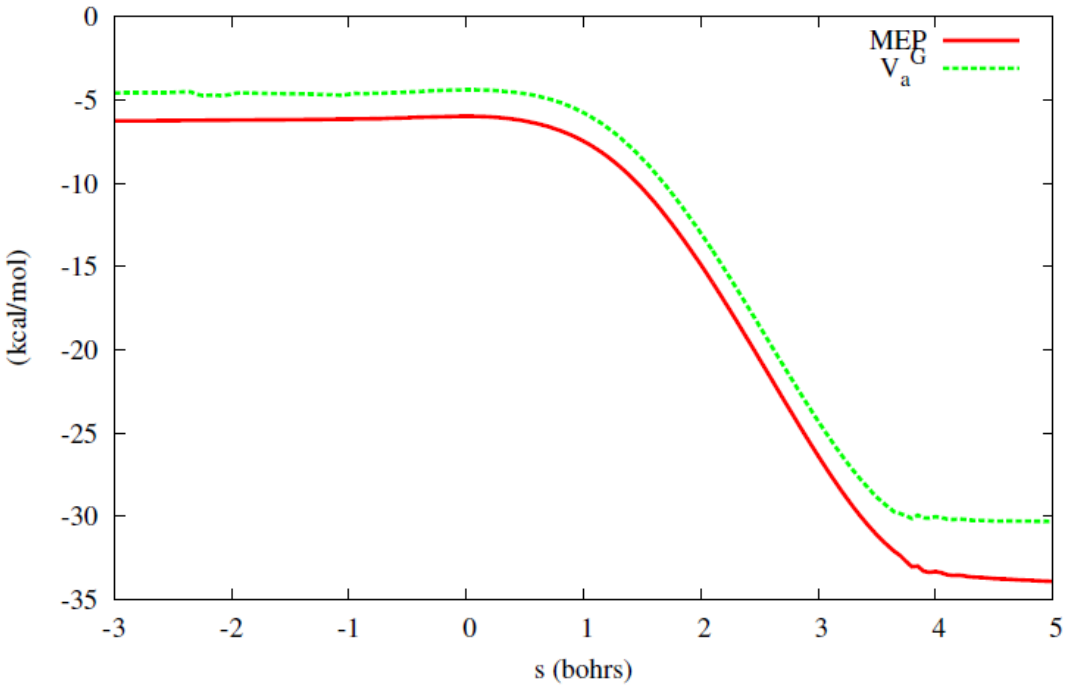

Figure S7. Minimum Energy Path (V_{MEP}) and Adiabatic (V_a^G) potential-energy profiles computed at M052X level of theory for the RAF mechanism between the C4 site of caffeic acid and the OH radical.

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